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(54) Title: **FURAN POLYMER IMPREGNATED WOOD**

(57) Abstract: A furan polymer impregnated wood which comprises wood impregnated with a polymerizable furfural alcohol monomer solution containing at least water, stabilizers, and furfuryl alcohol, and at least one further compound selected from the group consisting of anhydrides, acids and combinations thereof is described. A method for preparing a furan polymer impregnated wood and uses thereof is also described.

Furan polymer impregnated wood

The invention described herein relates to a furan polymer impregnated wood which is uniform in colour and density throughout the treated zone. In order to obtain the polymer impregnated wood, a parent wood has been impregnated with a
5 polymerizable furfural alcohol monomer solution containing at least water, stabilizers, and furfuryl alcohol, and at least one further compound. The invention also relates to a method for preparing a furan polymer impregnated wood and uses thereof.

Currently, wood is chemically preserved (protected from biodeterioration) mainly
10 by using toxic preservatives. Most of these preservatives also have toxicity to other organisms in the environment, including humans. Even if they are well-fixed in wood, their presence presents a problem for end-of-use. Two approaches which are designed to use more environmentally-friendly chemicals are i) use of water-soluble salts which have low toxicity and ii) use of non-toxic chemicals which
15 react with and alter the wood cell walls, making them less susceptible to biodeterioration.

Approach i) has the drawback that such salts usually leach out of wood in contact with water, limiting their usefulness. Boron and copper compounds have been used in this way. They have the advantage that some such salts act as fire retardants as
20 well as reducing biodeterioration.

An example of approach ii) is the subject of a previous invention disclosed by Schneider (NO-A-20005137) based on furfuryl alcohol (FA) treating formulations. This previous invention used an undiluted treating solution, and treated the wood
25 to high levels of retention. For woods with specific gravity near 0.30 (such as pine), the retention of chemical may approach 200% of the weight of the dry wood. For denser woods (about 0.60 specific gravity, such as maple and beech) retention can be in the 100% range. This level of retention has been shown to give excellent protection from biodeterioration, high dimensional stability in varying moisture conditions and an increase in most mechanical properties, particularly hardness.
30 The main disadvantage with this treatment is the large amount of chemical used and the resulting cost.

Furfuryl alcohol is highly water soluble and therefore easily forms a uniform
35 solution with water which can be used to impregnate wood. Therefore, FA impregnating solutions containing different amounts of water are easily made. However, there are things which must be overcome before a useful wood polymer composite can be made. First, after being impregnated into wood, the solution must

be polymerized to be useful. Second, the polymerization must occur in wet or dry wood. Third, the polymerization must occur at fairly low temperatures.

Chemical initiators therefore must be added to the FA to make it polymerize in the
5 desired temperature range and in wet or dry wood. How to initiate FA and make it
polymerize in the desired temperature range is known from NO-A-20005137.
However, the initiated FA from that technology does not mix well with water.
Combing them causes the mixtures to separate into two components which cannot
be uniformly impregnated into wood.

10 One object of the invention is to provide a furan polymer impregnated wood by
altering the wood cell wall with the same chemical monomer as that disclosed in
NO-A-20005137 but using smaller amounts of chemical.

15 Another object of the invention is to provide a uniform distribution of the
chemicals in the furan polymer impregnated wood which causes uniform colour
and density throughout the treated zone, by using water as an environmentally-
friendly and production-friendly diluent which would permit uniform but low
retention of active chemical in the treated zone of the wood.

20 Still another object of the invention is to provide a furan polymer impregnated
wood having improved properties as regards dimensional stability, rot resistance,
i.a.

According to the present invention, the foregoing and other objects are attained by
a product, method and uses thereof as disclosed in the patent claims.

25 In one embodiment of this invention, there is provided a furan polymer
impregnated wood, characterized by wood impregnated with a polymerizable
furfural alcohol monomer solution containing at least water, stabilizers, furfuryl
alcohol, and one further compound selected from maleic anhydride, phthalic
anhydride, maleic acid, malic acid, phthalic acid, and combinations thereof.

30 In another embodiment of this invention, there is provided a method for preparing
a furan polymer impregnated wood, characterized in that the wood is impregnated
by one impregnation step with polymerizable furfural alcohol monomer solution
containing at least water, stabilizers, and furfuryl alcohol, and at least one further
compound selected from the group consisting of anhydrides, acids and
35 combinations thereof, followed by a curing step.

In still another embodiment of the invention, there is provided use of a furan
polymer impregnated wood according to any of claims 1 to 7 or as manufactured

according to any of claims 8 to 12.

Two keys to the invention are 1) the use of one or more chemicals acting as new initiators and 2) the use of stabilizers which allows the initiated monomer to be water soluble. The initiators have similar affinity for wood as furfuryl alcohol and therefore enter the wood and remain in solution as deeply as it penetrates.

Wherever the solution penetrates, it is polymerizable. The initiators are selected from any anhydride-containing compound as well as acids selected from the group of maleic acid, malic acid, phthalic acid, and stearic acid. However, preferably a compound selected from maleic anhydride, malic anhydride, phthalic anhydride and combinations thereof is used. More preferably, maleic anhydride or phthalic anhydride or a combination thereof is used, most preferably maleic anhydride or phthalic anhydride. The stabilizers are borax and lignosulfonic acids. To make a treating solution, at least one of the initiators, preferably one of these initiators only, and both of the stabilizers are dissolved in water. Furfuryl alcohol is then added, forming a solution which has several months useful life at room temperature.

If limited surface impregnation or end-grain penetration is needed, brushing, rolling, spraying or soaking can be used.

For easily impregnable woods, when deep penetration is needed, vacuum only may be used. For deep and uniform penetration, there are three options: a) pressure alone (1 to 10 bar), b) vacuum followed by pressure (full cell process), c) atmospheric or low (1 bar) pressure followed by pressure and then final vacuum (empty-cell process).

For difficult-to-penetrate woods like spruce, an oscillating pressure method may be used.

Times of all of these processes depend upon many factors, including capability of equipment, size of wood, species of wood and penetration desired.

Impregnation method generally used (full cell process) in accordance with the present invention will depend on treatment loading desired, such as follows:

- i) loading vessel with wood and securing the load so it will not float (if using air pressure, i.e., not a fluid pressure pump system),
- ii) closing door and drawing an appropriate partial vacuum,
- iii) filling the vessel with the treating solution,
- iv) pressurizing the submerged wood to a pressure in the range of 7 to 10 bar (100-150 psi) depending on wood species or other factors. Pressurizing for 30 to 60 min.,

- v) after sufficient time under pressure, reducing pressure to 2 or 3 bar, and expelling the treating fluid with remaining pressure,
- vi) drawing a full vacuum in the treating vessel and holding for about 15 min.,
- vii) releasing vacuum and pressurizing to 2 bar,
- 5 viii) expelling the treating fluid (that was removed from cell lumens in step iv),
- ix) releasing all pressure, opening door and removing treated wood to curing area.

Wood moisture content must be below fiber saturation point (about 30% MC) in the zone to be treated. The further below, the more chemical which can be
10 impregnated. If a specific target amount of chemical is required, the moisture content of the wood and the amount of solution impregnated must be taken into account and the concentration of the treating chemical adjusted accordingly.

The treating solution is mixed and may contain, based on the weight of a given amount of water: borax (3%), maleic anhydride (2,3%), sodium salt of ligno-
15 sulfonic acid (5,5%), and furfuryl alcohol (30,0%).

The mixing operation is started by heating the water to approximately 60°C to facilitate the addition of borax, maleic anhydride and lignosulfonic acid components. When these solid additives are fully dissolved in the water, the solution is cooled to 20-25°C and then the furfuryl alcohol is blended in with
20 stirring, and is stored at a temperature of 15-20°C.

The curing can take place at a range of temperatures, starting at from about 25°C to about 140°C. The lower temperatures (below about 40°C) require a long time to cure (days or weeks). From about 70°C to about 100°C the curing time is hours. Above 100°C makes times even shorter but conditions are difficult because rapid
25 drying can occur and break the wood.

In accordance with the present invention steam or hot, humid air curing in the temperature range of about 70-100°C works well at a fixed temperature within the range. Also, temperature can be increased as curing and drying proceeds. Essentially, this is conventional temperature kiln drying operation. Curing and
30 drying in hot oil also works well at temperatures from 70 to 120°C, either a fixed temperature within the range or by increasing temperature within the range as curing and drying proceeds. The furfuryl alcohol will cure readily in this temperature range with the furfuryl alcohol/initiator ratio used. Material 10 to 20 mm thick will cure in just two or three hours, but drying to final moisture content takes longer.
35

The starting material is a woody material, usually lumber, which includes plank

(thick lumber), but can also be wood composites such as oriented strand board and particle board. Woody materials of any dimensions can be utilized.

The length of the woody materials is important since the treating solution travels very fast along the length but very slow across the cross-section. With permeable woods like beech and birch, the uniformity of treatment is determined by how well the treating solution remains uniform as it travels along the length. When impregnation is complete, the permeable woody material formed by this method has uniform properties throughout. Colour, resistance to moisture and deterioration and mechanical properties are consistent throughout. The properties and colour of individual pieces of lumber treated this way depend upon the loading of polymer achieved. Different species of wood, and even different boards of the same species, may impregnate differently. However, resistance to moisture and deterioration are little affected by loading.

Woody material, including cheap types and scrap material, can be used to produce noble wood products such as imitation teak, mahogany, and others, and also provide them with novel properties like water resistance and simpler and reduced maintenance requirements.

The following examples will further illustrate the invention.

Attempts were made to change the initiator types and amounts to obtain a combination that would result in a water-soluble, curable mixture with a useful shelf life. After many trials, two things became apparent:

1. Maleic anhydride (MA) was the best polymerization initiator. It is also a desirable component because it is thought to act as a bonding agent to wood.
2. Stabilizers were needed to keep the mixture uniform. Otherwise, it separated into two components and one settled to the bottom.
3. The pH must be near neutral for a uniform, stable mixture to be formed and maintained.
4. The pH must be on the acid side for curing to occur.

Surfactants and compatibilizers were tried as stabilizers. Borax (sodium tetraborate decahydrate) made homogeneous mixtures that penetrated wood well, and therefore became one of the stabilizers of choice. In some mixtures, stronger buffering to control pH using other compounds, such as sodium hydroxide, helped in maintaining a uniform mixture. Such compounds must maintain their buffering capacity until after the wood is impregnated. Then it is necessary for the pH to drop to facilitate curing.

The effects of varying MA initiator and borax stabilizer in the mixture on some physical properties of wood treated with them are given in Table 1.

5 Table 1. Monomer mixture concentrations and effects on wood properties.

	Treating formulation				Cured material							
	% added based on solution				% swell		% wt increase		% water swell		% ASE	
	FA	MA	Borax	Total	Pine	Beech	Pine	Beech	Pine	Beech	Pine	Beech
Water	0	0	0	0	1.7	2.2	-0.8	-0.4	9.8	17	0	0
Initiated FA	4.8	1.9	1.9	8.3	2.4	2.9	NA	NA	8.6	16	12	6
	9.1	2.7	2.7	13.8	3.0	3.6	8.2	6.3	7.3	15	26	12
	16.7	3.2	3.2	21.9	4.2	6.0	14.0	10.2	6.8	14	31	18
	23.1	3.7	3.7	28.6	5.7	7.0	20.5	14.6	6.3	12	36	29
	23.1	5.1	5.1	30.6	5.7	7.0	NA	NA	NA	NA	36	29
	28.6	4.1	4.1	34.2	6.9	7.1	26.9	17.6	4.6	13	53	24
	33.3	4.5	4.5	39.0	5.5	7.3	30.9	16.1	5.5	11	44	35
Initiated FA	93.9	6.5	0	NA	8.1	11.5	57.4	36.3	4.1	7	58	59

Note: Italic values are interpolated or calculated from interpolated values. Percent swell is the remaining swelling after curing. Percent weight increase is after curing. Water swell is maximum swelling in liquid water at 23°C and the ASE is anti-swell efficiency or percent retardation of swelling of the cured material in liquid water (based on the water swelling data).

To be useful, the mixture must impregnate and then cure throughout the wood, giving a uniform product. The monomer mixture containing 23.1% FA, and 5.1% each of MA and borax was selected for a uniformity-of-treating trial. The results are given in Table 2.

Table 2. Results treating samples for uniformity.

Scots pine samples					
Sample	% soln uptake	% poly uptake	Wt soln	Wt poly	% solids
1	146.2	37.9	14.58	3.78	20.6
2	138.8	38.0	14.69	4.02	21.5
3	151.0	38.9	14.92	3.84	20.5
4	147.0	41.7	14.67	4.16	22.1
5	152.1	38.3	15.00	3.78	20.1
6	140.4	41.2	14.59	4.28	22.7
7	165.3	48.3	15.44	4.51	22.6
8	147.9	41.6	14.89	4.19	22.0
9	143.9	40.4	14.95	4.20	21.9
10	148.9	44.0	14.71	4.35	22.8
	148.2	41.0	14.84	4.11	21.7

Beech samples					
Sample No.	% soln uptake	% poly uptake	Wt soln	Wt poly	
1	115.8	25.1	14.36	3.11	
2	118.2	25.6	14.24	3.09	
3	121.6	26.4	14.49	3.14	
4	113.9	24.7	14.21	3.08	
5	114.5	24.8	14.28	3.10	
6	112.3	24.3	14.09	3.05	
7	122.3	26.5	14.60	3.16	
8	111.4	24.1	14.30	3.10	
9	130.9	28.4	14.93	3.24	
10	127.7	27.7	14.95	3.24	
	118.8	25.8	14.45	3.13	
<i>Note: Weight is in grams, soln is solution (while still liquid) poly is polymer (after curing) and percent solids is the solution converted to polymer.</i>					

The concentration study showed that the solution introduced into wood at concentrations between about 8% and 39% progressively increase wood dimensions at impregnation, polymer loading and antiswell efficiency. The values for the concentration chosen for further work (31%) and the highest concentration water solution tested (39%) are compared to values for undiluted, initiated FA in Table 3.

Table 3. Relationship between maximum values (94% FA solution) and diluted (31% and 39% solution) values of wood properties.

% soln	Percent of maximum (94% FA)						
	Pine			Beech			ASE
	Swell	Polymer	ASE	Swell	Polymer	ASE	
31	70	NA	61	61	NA	50	
39	68	54	75	63	45	60	

These results show that for about 30% of the amount of polymer in wood that a full load would give results in material that has 60% of the resistance to swelling for a lower density wood (pine) and about 50% for a higher density wood (beech). Therefore the polymer present in the wood is more effective in preventing swelling than its amount would first suggest.

Decay resistance

The main reason for treating wood with this technology is to make it resistant to biodeterioration, especially decay caused by wood-rotting fungi. To test decay

5 resistance, samples 50 mm long and 15 mm by 25 mm in cross section were treated with a solution concentration of 23.1% FA, and 5.1% each of MA and borax. They were then exposed to various brown and white rot fungi according to European Standard EN113. Test results are given in Table 4.

10 Table 4. Decay test results

Pine samples					
Fungus	<i>Coniofora puteana</i>	<i>Poria placenta</i>	<i>Gleophyllum trabeum</i>	<i>Trametes versicolor</i>	
% wt loss	1.5	2.0	4.2		0.3
	5.7	-3.7	5.7		-1.4
	5.3	2.4	1.2		1.6
	6.6	-5.0	0.6		-1.3
	0.1	2.0	-2.0		0.9
	0.8	-3.1	-3.8		1.7
	1.3	2.2	0.9		-5.1
	0.8	-5.8	0.8		1.2
Average	2.8	-1.1	1.0		-0.3
Overall average					0.6
Beech samples					
Fungus	<i>Coniofora puteana</i>	<i>Poria placenta</i>	<i>Gleophyllum trabeum</i>	<i>Trametes versicolor</i>	
% wt loss	0.5	6.0	0.9		7.5
	2.4	3.1	4.8		3.7
	-2.1	3.8	5.9		3.5
	2.3	5.1	3.4		1.7
	1.0	-1.6	-2.9		0.1
	1.7	0.5	-1.3		0.3
	2.5	0.2	0.4		1.1
	5.8	2.9	-1.3		-1.8
Average	1.8	2.5	1.2		2.0
Overall average					1.9

The weight loss values for each fungus and both species allows the treated wood to be classed as «highly resistant» to decay according to Standard EN 113.

5 The solution of about 30% concentration was found to provide moisture and decay protection to the wood. However, other concentrations will also provide improved properties. To protect the ranges expected to be useful, the following water solution percentage limits are suggested:

FA		MA		Borax		NaOH	
Lower	Upper	Lower	Upper	Lower	Upper	Lower	Upper
2	90	2	5	1	5	1	5

CLAIMS

1. A furan polymer impregnated wood, characterized by wood impregnated with a polymerizable furfural alcohol monomer solution containing at least water, stabilizers, furfuryl alcohol, and one further compound selected from maleic anhydride, phthalic anhydride, maleic acid, malic acid, phthalic acid, and combinations thereof.
2. The furan polymer impregnated wood of claim 1, characterized in that said one further compound is maleic anhydride.
3. The furan polymer impregnated wood of claim 1, characterized in that said one further compound is phthalic anhydride.
4. The furan polymer impregnated wood of claim 1, characterized in that said one further compound is maleic acid.
5. The furan polymer impregnated wood of claim 1, characterized in that said one further compound is malic acid.
6. The furan polymer impregnated wood of claim 1, characterized in that said one further compound is phthalic acid.
7. The furan polymer impregnated wood of any of the preceding claims, characterized in that the stabilizers are borax and sodium salts of lignosulfonic acids.
8. A method for preparing a furan polymer impregnated wood, characterized in that the wood is impregnated by one impregnation step with polymerizable furfural alcohol monomer solution containing at least water, stabilizers, and furfuryl alcohol, and at least one further compound selected from the group consisting of anhydrides, acids and combinations thereof, followed by a curing step.
9. The method of claim 8, characterized in that said curing is performed by use of a temperature in the range of from about 70 to about 140°C.
10. The method of claim 9, characterized in that said curing requires conventional kiln drying using the normal temperature schedules for drying untreated, green lumber of the same size and species as the impregnated material, with temperatures at the beginning of curing about 70°C and at the end about 80°C, with a final post-curing step between 100 to 120°C for material with maximum hardness and dryness.

11. The method of claim 10, characterized in that said curing and drying can be accomplished using high-temperature kiln schedules in the 80 to 120°C temperature range.

12. The method of claim 11, characterized in that curing is performed by
5 submerging the treated material in hot oil, preferably 80 to 120°C, with the temperature either fixed or starting lower in the range and increasing as curing and drying proceeds.

13. Use of a furan polymer impregnated wood as prepared according to claims
8 to 12, as building parts (facia, cornice, siding, sills, frames, millwork), boat parts
10 (frames, planking, decks), marine items (docks, piers, lobster traps, weir poles), outdoor items (furniture, decks, railings and stairs, walkways, boardwalks, playground equipment), bridge parts (beams, railings, decking), railway sleepers, cooling tower slats, utility poles, heavy timbers, fenceposts, stakes, highway items (guard rail posts, guard rail plates, sign posts, light poles) and container (tanks,
15 buckets.

INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

IPC7: B27K 3/50, B27K 3/38, B27K 3/15

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: B27K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	STN International, File CAPLUS, CAPLUS accession no. 1996:412339, Westin, M. et al: "New chemicals for wood preservation and new ways of chemical modification"; & Book of Abstracts, 212th ACS National Meeting, Orlando, FL, August 25-29 (1996), CELL-006 Publisher: American Chemical Society, Washington, D. C. --	1-13
Y	US 3622380 A (FREDRICK D. WILLIAMS), 23 November 1971 (23.11.71) --	1-13
Y	US 2909450 A (IRVING S. GOLDSTEIN), 20 October 1959 (20.10.59) --	1-13

 Further documents are listed in the continuation of Box C. See patent family annex.

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INTERNATIONAL SEARCH REPORT

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4678715 A (EBERHARD GIEBELER ET AL), 7 July 1987 (07.07.87) -- -----	1-13

INTERNATIONAL SEARCH REPORT

Information on patent family members

01/05/02

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Patent document cited in search report	Publication date	Patent family member(s)		Publication date
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US 2909450 A	20/10/59	NONE		
US 4678715 A	07/07/87	AT 35103 T DE 3504898 A DE 3563321 D EP 0191196 A,B FI 80625 B,C FI 860569 A JP 61188101 A	15/07/88 14/08/86 00/00/00 20/08/86 30/03/90 14/08/86 21/08/86	